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AFRPL-TR-67-113

AD385405

(Unclassified Title)

INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PROPELLANT INGREDIENTS AND THE BURNING MECHANISMS OF PROPELLANTS

QUARTERLY PROGRESS REPORT AFRPL-TR-67-113

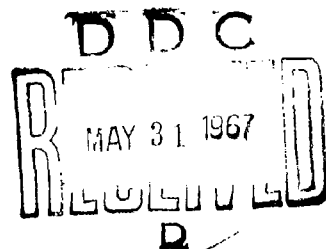(1 January 1967 to 31 March 1967)

APRIL 1967

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

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Report Nr. T-0025-1Q-67

QUARTERLY PROGRESS REPORT (U)

(1 January 1967 to 31 March 1967)

April 1967

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
CONTRACT NR. FO4611-67-C-0025

SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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ABSTRACT

(C)   Work on the heat of hydrolysis of lithium-doped crystalline beryllium hydride has been completed.

(C)   The composition of the sample from analytical data was 88.7 weight per cent BeH_2. After correction for impurities, the hydrolysis experiments yielded a heat of formation of -5.25 kcal/mole. As expected, this value is slightly more negative than -4.5 kcal/mole previously found for amorphous BeH_2.

(U)   A preliminary value for the heat of formation of gaseous CF_3ONF_2 was derived from the heat of explosion of mixtures of the sample and hydrogen. The result, -188.4 ± 2.0 kcal/mole, is about the expected value for this compound.

(C)   Work on DAHTP from Thiokol Corp., TVOPA from Rohm and Haas Co., and "liquid Be polymer" from Rocketdyne Corp. is continuing.

(U)   In the synthesis work, the purification of TVOPA has been continued and a method has been developed which gives satisfactory results. Additional pure CF_3ONF_2 has been prepared for heat of formation measurements. A synthesis procedure for CF_3NF_2 has also been developed.

(U)   The volatilization and combustion of elemental boron has been studied by flash pyrolysis - kinetic spectroscopy. The species B and B_2 were detected during the volatilization of the element. The combustion of boron in oxygen showed the presence of BO, BO_2, B_2O_2 and B_2O_3 during the reaction.

(U)   The flash pyrolysis of $H_3BO_3(HOBO \cdot H_2O)$ showed the presence of OH, and BO_2 indirectly that the species HOBO may dissociate to H and BO_2 at high temperatures.

(U)   There is some evidence that B_2O_3 dissociates to BO and BO_2 at temperatures above its boiling point.

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the first quarterly report, covering the work performed during 1 January 1967 through 31 March 1967. The Dow Report Number is T-0025-1Q-67.

The work was performed by C. E. Merrill, R. V. Petrella, G. C. Sinke, A. C. Swanson, and L. C. Walker under the technical supervision of Dr. D. R. Stull and Dr. D. A. Rausch, and management supervision of Dr. R. P. Ruh.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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SECTION I

THERMOCHEMISTRY

A. HEAT OF FORMATION OF LITHIUM-DOPED BERYLLIUM HYDRIDE (C)

1. Introduction (U)

(C) A sample of lithium-doped beryllium hydride was furnished by Dr. Fred W. Frey of Ethyl Corporation. The sample was characterized by Ethyl Corporation as follows:

Ethylane Sample No. E-166

Constituent:

Purity[a]	91.4%
Beryllium Metal	1.4%
Beryllium Alkyls[b]	
C_4	0.7%
C_3	0.0%
C_2	0.7%
Lithium[c]	1.4%
Chloride	0.31%
Beryllium Alkoxides	0.11%
Carbon	1.17%
Hydrogen	16.91%
Absolute Density	0.76 g/cc

X-Ray Phase 378-295 - 60%
      Phase 338-208 - 40%

(a) Purity is average of deuterolysis and carbon-hydrogen, assuming all hydridic hydrogen bound to beryllium, none to lithium.

(b) All alkyls assigned to beryllium.

(c) Probably present as lithium hydride or lithium beryllium tetrahydride.

(C) The heat of formation of this crystalline beryllium hydride was derived from measurements of the heat of solution in hydrochloric acid. Analytical data agree in general with those of Ethyl Corporation, but differ in some quantitative aspects.

2. Equipment (U)

(U) A rotating bomb calorimeter and a platinum-lined rotating bomb were used for the calorimetry. An automatic bridge developed under a previous contract was employed for the time-temperature curves. The calorimeter was calibrated by combustion of NBS

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standard samples of benzoic acid. The value obtained for E
(calor.) was 3426.85 cal/°C with a standard deviation of 0.01%.

3. Procedure (U)

(C) A thin walled glass bulb was filled with 7.26 N HCl,
sealed off, and placed in the platinum-lined bomb. The bomb was
closed and thoroughly flushed with dry prepurified nitrogen. The
bomb was locked into a dry box and opened. An analytical balance
in the dry box was used to weigh out an appropriate amount of
beryllium hydride which was then added to the bomb. The bomb
was closed, removed from the dry box and placed in the calorim-
eter. After initial drift rate readings were taken, rotation of
the bomb was started. The tumbling glass bulb broke open and
reaction took place. After completion of the calorimetric read-
ings, the bomb gases were analyzed by combustion to CO_2 and H_2O
and adsorption in Ascarite and magnesium perchlorate. The bomb
solution was recovered and analyzed for beryllium and lithium.

(C) To eliminate any systematic errors, the same procedure
was used for the heat of solution of a sample of beryllium metal.
The difference between heats of solution of the hydride and the
metal is a measure of the heat of formation of beryllium hydride.

4. Analytical Results (U)

(C) A summary of the analytical data for the beryllium hy-
dride is given in Table I. The interpretation of these results
is arbitrary. The results of both Ethyl Corporation and Dow
were used to arrive at the proposed composition given in Table II.
The calculated elemental composition compares well with the experi-
mental results of Table I. There is also good agreement with
Ethyl Corporation data except that our total hydrogen, as well as
our hydridic hydrogen, is slightly lower.

(U) Two samples of beryllium metal were used. A sample ob-
tained from Electronic Space Industries, Inc., was found to con-
tain 1.5% oxygen and gave erratic heat of solution results. A
second sample obtained from United Minerals and Chemicals Cor-
poration contained 0.012% oxygen by neutron activation analysis.
X-Ray fluorescence analysis of this second sample indicated no
other metals present in amounts greater than 0.001% each. The
total metallic impurity was indicated as less than 0.01%.

5. Calorimetric Results (U)

(U) The results of five successful experiments on beryllium
metal are given in Table III. The sample weight was corrected
to mass in vacuo. The density of beryllium was taken as 1.85 g/cc.
The product of the calorimeter equivalent and the corrected tem-
perature rise gives the total calories absorbed by the system.
Additional heat was absorbed by the glass bulb, the acid, beryl-
lium metal, platinum added to the system, and one atmosphere of

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Table I

(C)   Analytical Data for Beryllium Hydride (Sample E-1..)

Element	% of Sample	Analysis Technique
Chlorine	0.29 ± 0.03	Neutron activation
Oxygen	4.44 ± 0.01	Neutron activation
Copper	0.10 ± 0.01	Neutron activation
Manganese	Negligible	Neutron activation
Iron	Negligible	Neutron activation
Beryllium	75.6 ± 0.2	Precipitation of BeO from bomb solutions, firing at 1000°C. and weighing
Lithium	1.34 ± 0.04	Atomic absorption analysis of bomb solutions after removal of beryllium
Total Carbon	1.76 ± 0.1	Direct combustion of sample in oxy-
Total	16.60, 16.73	gen and absorption of CO_2 and H_2O
Carbon	1.16 ± 0.02	Combustion of bomb gases formed by
Hydrogen	33.20 ± 0.06	hydrolysis and absorption of CO_2 and H_2O
Carbon	0.32	Carbon in bomb solutions formed by hydrolysis and analyzed by a combustion-infrared method

Table II

(C)   Proposed Composition of Beryllium Hydride (Sample E-166)

Molecular Composition	Calculated Elemental Analysis for this Composition, %
0.125 CuO	0.10 Cu
0.327 $BeCl_2$	0.29 Cl
1.535 LiH	4.32 O
0.775 $Be(C_2H_5)_2$	1.34 Li
0.775 $Be(C_4H_9)_2$	75.62 Be
0.110 $Be(OC_2H_5)_2$	16.74 H
6.463 BeO	1.59 C
88.740 BeH_2	
0.560 Be	1.16 C (gas phase)[a]
0.590 Residual ether or solvent	33.23 H (gas phase)[b]

[a] Assuming only the beryllium alkyls contribute to gas phase carbon gives 1.16% C.

[b] Assuming LiH, BeH_2, Be, and beryllium alkyls contribute to gas phase hydrogen gives 33.23% H.

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Table III

(U)   Heat of Solution of Beryllium in 7.26 N HCl

| | Experiment Number | | | | |
	1-A	2-A	3-A	4-A	5-A
Be mass, g	0.38219	0.40458	0.40693	0.40692	0.40296
Δt_c, °C	1.10309	1.16731	1.17266	1.17289	1.16300
$\epsilon \Delta t_c$, cal	3780.12	4000.20	4018.53	4019.32	3985.43
ΔE glass, cal	0.72	0.59	0.55	0.62	0.61
ΔE_{HCl}, cal	18.12	20.28	20.51	20.36	20.17
ΔE_{Be}, cal	0.18	0.21	0.21	0.21	0.20
ΔE_N, cal	0.07	0.08	0.08	0.08	0.07
ΔE_{Pt}, cal	0.05	0.05	0.05	0.05	0.05
Vaporization corr., cal	2.15	2.15	2.15	2.15	2.15
$-\Delta E_R/M$ cal/g	9946.4	9945.0	9933.1	9935.1	9948.1

Average $-\Delta E_R/M$ = 9941.5 cal/g
  BeO correction = 0.1
  Corrected sample mass = 0.9998 g
Corrected $-\Delta E_R/M$ = 9943.4 cal/g

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nitrogen in the bomb. Heat capacity values for these substances are given in Table IV. The vaporization correction is due to the vaporization of water and HCl into the dry atmosphere of the bomb. The average $-\Delta E_r/M$ for the five runs is corrected for 0.02% BeO to yield for the process (Be at. wt. = 9.0122):

$$Be(c) + 2HCl \text{ (1 in 6.52 HCl)} \rightarrow BeCl_2 \text{ (in aq HCl)} + H_2(g)$$
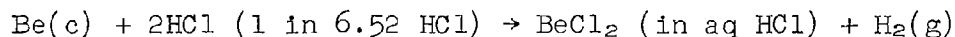
$$\Delta E_r = -89.61 \text{ kcal/mol}$$

$$\Delta n(g) = +1, \quad \Delta nRT = +0.59 \text{ kcal/mol}$$

$$\Delta H_r = -89.02 \text{ kcal/mole}$$

Table IV

(C) Heat Capacity of Bomb Contents

Substance	Cp, cal/g°K
Pyrex glass	0.17
7.26 N HCl	0.685
Platinum	0.0317
Nitrogen	0.178
Beryllium	0.436
Beryllium hydride	0.60

(C) The results of five successful runs on beryllium hydride are given in Table V. The density was taken as 0.76 g/c. to correct weights to mass in vacuum. Additional heat terms for bomb contents were calculated as for the beryllium metal runs. Heat capacity data are listed in Table IV. The vaporization correction is the same as for the beryllium runs, since the ratio of acid to sample was adjusted to make the final solution for the two sets of experiments identical. The average $-\Delta E_r/M$ for the five runs is adjusted for impurities by means of data given in Table VI. The final value for pure crystalline beryllium hydride applies to the process (BeH₂ mol. wt. = 11.02814):

$$BeH_2(c) + 2HCl \text{ (1 in 6.52 HCl)} \rightarrow BeCl_2 \text{ (in aq HCl)} + 2H_2(g)$$
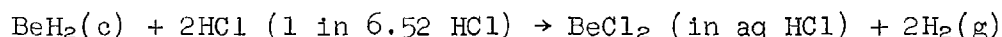
$$\Delta E_r = -84.95 \text{ kcal/mol}$$

$$\Delta n(g) = +2 \quad \Delta nRT = +1.18 \text{ kcal/mol}$$

$$\Delta H_r = -83.77 \text{ kcal/mole}$$

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Table V

(C) Heat of Solution of Beryllium Hydride in 7.26 N HCl

	Experiment Number				
	1-A	2-A	3-A	4-A	5-A
BeH_2 mass, g	0.5497	0.5200	0.5243	0.5162	0.5446
Δt_c, °C	1.12200	1.05981	1.06735	1.05780	1.11492
$\varepsilon \Delta t_c$, cal	3844.93	3631.81	3657.65	3624.92	3820.66
ΔE glass, cal	0.60	0.55	0.54	0.60	0.56
ΔE_{HCl}, cal	19.74	18.02	18.37	18.10	19.44
ΔE_{BeH_2}, cal	0.37	0.33	0.34	0.33	0.36
ΔE_N, cal	0.07	0.07	0.07	0.07	0.07
ΔE_{Pt}, cal	0.05	0.05	0.05	0.05	0.05
Vaporization corr., cal	2.15	2.15	2.15	2.15	2.15
$-\Delta ER/M$	7036.4	7025.0	7017.3	7063.6	7057.1

Average $-\Delta ER/M = 7039.88$ cal/g

Corrections in Calories

```
CuO  - - - - - -  0.17
BeCl₂ - - - - -  1.88
LiH  - - - - - - -89.03
BeO  - - - - - - -36.71
Be(C₂H₅)₂ - - -13.25
Be(C₄H₉)₂ - - - 7.43
Be(OC₂H₅)₂- - - 0.14
Be- - - - - - -55.68
```

Corrected sample mass = 0.8874 g

Corrected $-\Delta E_R/M = 7702.9$ cal/g

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Table VI

(U) Heat of Reaction of Impurities with 7.26 N HCl

Impurity	$-\Delta E_r/M$, cal/g
CuO	137
BeCl$_2$	576
LiH	5800
BeO	568
Be(C$_2$H$_5$)$_2$	1710
Be(C$_4$H$_9$)$_2$	958
Be(OC$_2$H$_5$)$_2$	124
Be	9943

(C) Combining this result with the previous value for beryllium metal yields for the hydride:

$$\Delta Hf^\circ_{298}(BeH_2, c) = -5.25 \text{ kcal/mol}$$

(U) The uncertainty is difficult to assess because of the large impurity corrections, but does not appear likely to exceed ± 1 kcal/mol. The result obtained for this crystalline sample is only slightly more negative than -4.5 kcal/mol obtained earlier in this laboratory for an amorphous sample.

B. WORK IN PROGRESS (U)

1. Trifluoromethoxydifluoroamine, CF$_3$ONF$_2$ (U)

(U) Several runs were completed on the heat of explosion of CF$_3$ONF$_2$ mixed with H$_2$. The products of the reaction were CO(g), N$_2$(g) and HF(aq). Analyses for CO and HF both ran about 1% low, indicating either an impurity or errors in procedure. A preliminary value for the heat of formation of CF$_3$ONF$_2$(g) was derived at -188.4 ± 2.0 kcal/mol. Further work is planned on this material.

2. Diammonium Hydrazinium Tetraperchlorate (DAHTP) (C)

(C) A crystalline solid material (code DAHTP) was furnished by Thiokol Chemical Corporation. This sample was analyzed for hydrazine and ammonia content and found to be better than 99.5% pure. Since the heats of formation of the individual components of the double salt are known, a simple heat of solution determination should give a reliable heat of formation. Work on this has been initiated.

3. 1,2,3-tris[bis-α,β-(Difluoroamino)ethoxy]propane (TVOPA) (U)

(U) Work on evaluation of various purification techniques is continuing in cooperation with the synthesis effort. Specifically, samples are burned in a platinum-lined combustion bomb to determine the heat of combustion, and the bomb solution is recovered for chloride analysis. No fully satisfactory purification procedure has yet been found.

4. Liquid Beryllium Hydride Polymer (C)

(U) A sample of this material has been received from Rocketdyne Corporation and heat of hydrolysis measurements are in progress.

C. TRIP (U)

(U) Mr. Arlo Swanson attended the ICRPG Working Group on Thermochemistry Meeting held at Esso Research on March 15 and 16. He presented a paper reviewing thermochemical results obtained at the Dow Thermal Laboratory in the past year.

D. SYNTHESIS (U)

1. Discussion (U)

(C) Work toward removal of solvent from material TVOPA has continued. A new lot has been obtained in which the solvent is a mixture of 65% chloroform and 35% Freon 113, and as a result, previous techniques for removing methylene chloride solvent were inadequate. After small amounts of impurities were removed by elution of pure material with a 50% benzene-50% methylene chloride mixture from an acid washed silica gel column, the solvent was removed by high vacuum (<10 μ) on a Rotovac apparatus. This procedure appeared to give satisfactory results.

(U) The preparation of pure CF_3ONF_2 was continued due to unexpected difficulties. About six more grams have been prepared and purified by previously reported techniques and have been supplied to the Thermal Research Laboratory for completion of their work.

(U) Exploratory work toward the synthesis of CF_3NF_2 has indicated that the following reaction is satisfactory.

$$CF_3I + N_2F_4 \xrightarrow[\text{Corex Filter}]{h\nu} CF_3NF_2 + \text{Side products} \ (\sim 50\% \text{ conv.})$$
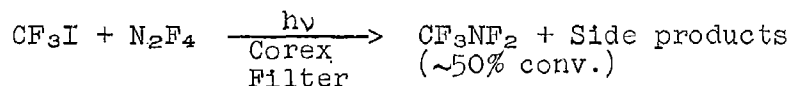
(U) Side products consisted of CF_4, NF_3, I, N_2O, and SiF_4. They were removed by codistillation and by passing the mixture through either an Ascrite or solid potassium hydroxide bed. A final gas chromatographic procedure gave about three grams of fairly pure material. The purity was based on the infrared spectrum and the gas chromatogram.

Future work will involve continued purification of material TVOPA, preparation and purification of additional amounts of CF_3NF_2, and preparation and purification of diborane.

2. Experimental

Into a 5-liter flask was vacuum transferred 5.8 g. (0.03 mole) of CF_3I and 3.15 g. (0.03 mole) of N_2F_4. This mixture was irradiated for 24 hours with an immersion ultraviolet lamp surrounded by a 9700 Corex glass filter (eliminates wavelength below 260 millimicrons). The crude product was codistilled to remove the bulk of impurities, then it was passed through a bed of KOH pellets where most of the remaining SiF_4 was removed. Subsequent gas chromatography through a 21-ft. Kel-F tetramer column (25% oil on Chromosorb W) at -65°C. gave 1.82 g. (50% of theory) of pure material.

SECTION II

COMBUSTION KINETICS

A. INTRODUCTION

The combustion of elemental boron in air or oxygen has long been an anomalous phenomenon. The primary physical parameters of boron combustion are due to the fact that the melting point, and especially the boiling point, of the metal exceed the boiling point of the boric oxide (B_2O_3), which is the ultimate product of the combustion. The high vapor pressure of the oxide at the ignition temperature of boron in oxygen $(2200°K)$[1] places boron in the realm of a surface burning metal, in contrast to aluminum, which burns primarily in the gas phase[2]. Table VII shows the melting and boiling points of boron and some of its oxidation products.

Table VII

Physical Properties of Boron, Its Oxides and Acids[a]

	M.P., °K	B.P., °K
Boron	2450 ± 20	3931 (estimate)
HBO_2	509 ± 1	Sublimes
H_3BO_3	441.1 ± 0.2	Dissociates at 330
B_2O_3	723 ± 2	2316

[a]JANAF Tables

It can be seen from Table VII that the melting point of elemental boron is higher than the boiling point of any of its reaction products. In fact, the products H_3BO_3 and HOBO dissociate below 600°K.

The inefficiency in the combustion of elemental boron, as well as in the borane fuels, has been attributed to the formation of HOBO. The first definite evidence for the existence of gaseous HOBO at high temperature was the infrared emission studies of White, Mann, Walsh and Sommer[3]. From the intensity vs. temperature variation of the 2030 cm^{-1} band, the heat of reaction for:

$$1/2\ B_2O_3(1) + 1/2\ H_2O(g) = HBO_2(g) \qquad (1a)$$
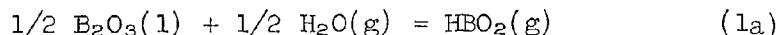
was found to be 39.0 ± 2.5 kcal/mol at 1350°K, corresponding to a $\Delta Hf°$ of -135.0 ± 3.0 kcal/mol for $HBO_2(g)$. This work has led to the assertion that the formation of HBO_2 is an endothermic process. Using the latest JANAF data, a heat of reaction of

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+36.6 kcal/mol is calculated if the B_2O_3 is liquid at 2500°K. The temperature is approximately that calculated for the flame temperature of elemental boron in oxygen. In fact, Fassell et al.[4] calculated an adiabatic flame temperature at 3786°K for the combustion of boron to B_2O_3 in oxygen.

There is some doubt that the actual process in a rocket combustion is simulated by this static equilibrium experiment. Accepting Talley's work at Experiment Inc., that the flame temperature of elemental boron combustion is equal to the oxide boiling point, 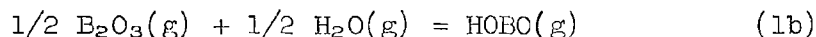then we could conclude the primary reaction between B_2O_3 and water is a homogeneous gas phase reaction since the gaseous H_2O would first come in contact with gaseous B_2O_3. JANAF Table data show that this reaction:

$$1/2 \ B_2O_3(g) + 1/2 \ H_2O(g) = HOBO(g) \qquad (1b)$$

is exothermic by 6.7 kcal/mol.

There is some reason to doubt that the formation and existence of HOBO is detrimental. Another possibility for the low combustion efficiency of boron containing fuels could be the dissociation of B_2O_3 via:

$$B_2O_3(g) = BO(g) + BO_2(g) \qquad (2)$$
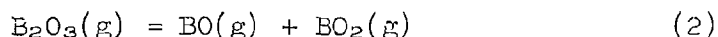
Calculation shows the above reaction to be endothermic by 131 kcal/mol at 2500°K.

The gas phase reaction is discussed for two reasons. First, it is recognized that problems are encountered with the oxide layer surrounding a burning boron particle, and this effect will not be discussed again. The problems associated with the low efficiency combustion characteristics of elemental boron may be due largely to this. However, this oxide layer effect does not exist in the combustion of volatile boron fuels (boranes, borazines, etc.), while the low combustion efficiency does still exist, indicating, perhaps, a gas phase combustion problem. Second and more important from an experimental point of view, the flash heating apparatus "sees" only gas phase products which have electronic spectra. In reporting data on the combustion of elemental boron, species which cannot be detected by the apparatus are not ruled out, but the investigation will be concentrated mainly on these species which can be identified.

B. EXPERIMENTAL

The flash heating apparatus employed in the present work has already been described[5]. It was employed to study the combustion of LMH-2 on Contracts AF 04(611)-7554 and AF 04(611)-11202.

The boron used in the present work is "Avco 400." The elemental analysis of the metal is:

$$B = 89.75\% \text{ (avg. of 90.0\% and 89.5\%)}$$
$$C = 0.95\%$$
$$H = 0.76\%$$

The remainder is B_2O_3.

The oxygen used in the combustion studies was Dow oxygen of 99 mole percent purity. The H_3BO_3 used in supplementary studies was obtained from Jarrell-Ash Company and showed only 1 ppm of magnesium as an impurity. The studies carried out on B_2O_3 employed an oxide obtained for Matheson-Coleman and Bell. This material was of at least 99 mole percent purity.

The first study undertaken was on the volatilization of the elemental boron to determine which absorption lines of the element were present.

The next study, which is still under investigation, deals with the gas phase products from the reaction between liquid and gaseous boron and oxygen. These studies were carried out at an oxygen pressure of 30 mm, although a few reactions were carried out at 20 mm oxygen. The delay time ranged from 14 to 3000 μsec at 1500-2000 joules.

Since one of the high temperature products of the oxidation of boron in a B-O-H system is HOBO, a study was undertaken to determine modes of dissociation and oxidation of this species. The HOBO was prepared _in situ_ from the thermal dissociation of H_3BO_3 by the reaction:

$$H_3BO_3(s) = HOBO(s) + H_2O(g) \tag{3}$$
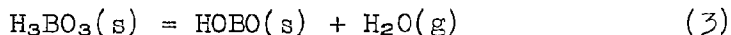
at about 330°K as per the JANAF Tables. The boric acid, H_3BO_3, was flash pyrolyzed both in a vacuum and at 30 mm oxygen at 1815 joules (11.0 KV and 30 μfd). The delay range was varied from 54 to 500 μsec.

Studies were also carried out on the flash pyrolysis of B_2O_3 to determine the extent of reaction (2). The oxide was pyrolyzed both in a vacuum and at 50 mm oxygen pressure at flash energies between 1815 and 2160 joules and at delays between 105 and 1500 μsec.

C. RESULTS AND DISCUSSION

1. Pyrolysis of Elemental Boron

The pyrolysis of elemental boron was studied at 1815 joules for the time delay of only 0 to 210 μsec. No attempt was made to study the volatilization at longer delay, since it was desired

only to identify boron lines. If the combustion of boron is as slow as is expected, the lines should be present in greater intensity at longer delays. The purpose of this study was to determine the time delay for the first absorption boron lines. The shortest line delay at which boron lines were seen was 105 μsec. The lines identified were the 2486.8 Å and the 2497.7 Å lines of BI. Also seen were the 0-0 lines of the $^3\Sigma \leftarrow \Sigma g$ transition of the diatomic molecule B_2 at 3272.8 Å and the 3-3 bands of the same transition at 3300.4 Å[6].

In subsequent studies described below, additional lines of B_2 were identified. The present study proved that elemental boron could be volatilized in the flash heating apparatus and its gas phase products identified. Once the gaseous species B and B_2 are detected, it could be concluded that some part of the boron combustion, small though it may be, is a homogeneous gas phase reaction.

2. Combustion of Boron in Oxygen

The first thing that is noticed in the combustion of boron in oxygen is the multitude of lines seen in absorption. These incluse OH (from the "glue" used to adhere the boron to the graphite strips plus that from the 0.76% H_2 in the boron itself), α-BO, β-BO, BO_2, B_2O_2, BH, and the species NH and CN, from the volatilization of the graphite strips and their subsequent reaction with the adsorbed nitrogen from the dry box. One spectrum, for example, contained 265 absorption lines between 3000 and 4500 Å.

The α-BO absorption lines were identified from the work of Mulliken[7] and Jenkins and McKellar[8]. The β-BO spectrum was compared to that reported by Mulliken[7] and by Lagerqvist, Nilsson and Wigartz[9].

The BO bands, both α- and β-systems, were intense. The α-bands were the 1-1 band at 4363 Å; the 2-0 band between 3838 and 3846 Å. The β-BO bands identified were the 0-4 band with the head at 2810 Å, the 1-5 band at 2851 Å, and the 3390 Å band of the 2-9 absorption. The high ν'' values of the BO bands indicate the extreme thermal effects of the combustion.

The BO_2 could be accounted for by the reactions:

$$BO + O_2 = BO_2 + O \qquad (4)$$

or

$$BO + O \xrightarrow{M} BO_2 \qquad (5)$$
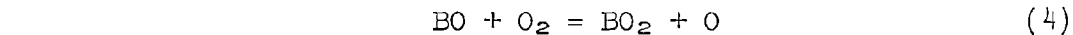
The spectrum was identified with the aid of the bands reported by Johns[10]. The intensity of the BO_2 lines increases as the oxygen pressure is raised from 20 to 30 mm.

The species B_2O_2 was identified by the absorption at 4292, 4346, and 4355 Å, respectively. These bands correspond well to

-13-

those reported by Porter and Dows[11]. The intensity of the B_2O_2 lines is greatest early in the reaction, indicating it might be

$$B_2 + O_2 \xrightarrow{M} B_2O_2 \qquad (6)$$
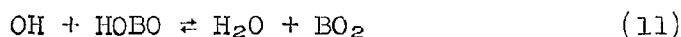
or

$$BO + BO \xrightarrow{M} B_2O_2 \qquad (7)$$

The species BH was identified through the absorption at 3396 Å, 3682-3745 Å, and especially from the lines 4319, 4331, and 4333 Å of the $'\pi \longleftarrow {}'\Sigma$ transition[12,13]. The source of the hydrogen for the BH is most likely to be found in the hydrocarbon "glue" used to adhere the boron to the graphite strips.

As reported above, this boron-oxygen reaction has been studied only for delay times as long as 3000 μsec. The very complex spectrum of the boron-oxygen system suggested that many of the early combustion products (H_3BO_3, HOBO, BO_2, etc.) were dissociating in the first 1000 μsec, while at the same time the bulk of the elemental boron was just beginning to burn. The proliferation of B-H-O species early in the reaction (0-1000 μsec), as well as the predominance of BO at longer times, suggests that indeed the first products of the combustion dissociate early in the reaction.

3. Reactions of HOBO and H_3BO_3

The role of HOBO has been thought to be that of a heat-sink such as Reaction (1a). In order to ascertain the absorption lines due to the reaction of HOBO, H_3BO_3 (HOBO·H_2O) was pyrolyzed and its spectrum analyzed.

The spectra of OH and BO_2 were seen in greatest intensity. Since BO_2 was seen prior to BO, the following scheme for the dissociation of HOBO is suggested:

$$H_3BO_3 \xrightarrow[\Delta]{h\nu} H_2O + HOBO \qquad (8)$$

$$H_2O \longrightarrow H + OH \qquad (9)$$

$$HOBO \longrightarrow H + BO_2 \qquad (10)$$

$$OH + HOBO \rightleftarrows H_2O + BO_2 \qquad (11)$$

and finally

$$BO_2 + H \longrightarrow BO + OH \qquad (12)$$

and

$$BO_2 + BO \longrightarrow B_2O_3 \qquad (13)$$
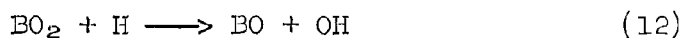
It is important to note that the results suggest, at least under our experimental conditions of vacuum pyrolysis, that the O-H bond of HOBO is ruptured, not the O-B bond.

The combustion of H_3BO_3 in 30 mm of oxygen showed the same lines to be present but of a greater intensity. This tends to

indicate that the combustion of HOBO proceeds via the OH radical arising from:

$$H_2O + O_2 \longrightarrow 2OH + O \qquad (14)$$

and

$$HOBO + O \longrightarrow OH + BO_2 \qquad (15)$$

Additional studies will be carried out on HOBO and H_3BO_3 as the need becomes apparent.

4. High Temperature Reactions of B_2O_3

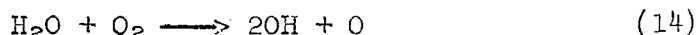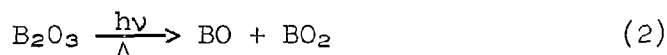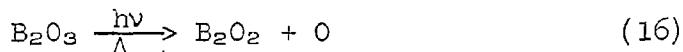The high temperature vacuum pyrolysis of B_2O_3 has not yet been analyzed in detail. However, the species BO, B_2, and BH were seen when B_2O_3 was flashed. No BO_2 has been detected. Until a careful analysis is carried out, Step (2):

$$B_2O_3 \xrightarrow[\Delta]{h\nu} BO + BO_2 \qquad (2)$$

cannot be eliminated as possible reaction step in favor of:

$$B_2O_3 \xrightarrow[\Delta]{h\nu} B_2O_2 + O \qquad (16)$$

$$B_2O_2 \longrightarrow B_2O + O \qquad (17)$$

$$B_2O \longrightarrow BO + B \qquad (18)$$

G. S. Bahn, at the 1966 Spring Meeting of the Western States Section of the Combustion Institute, suggested the possibility of the species B_2O playing a prominent role in the combustion of boron[14]. A series of lines in the range 3500-3770 Å cannot be identified. These lines decrease in intensity as the pressure of oxygen is increased. The same type of behavior would be expected from B_2O, as oxygen would cause it to react to B_2O_2 and B_2O_3 via:

$$B_2O + O_2 = B_2O_2 + O \qquad (19)$$

and

$$B_2O_2 + O = B_2O_3 \qquad (20)$$
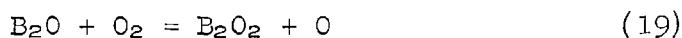
For a more detailed treatment of the formation of B_2O from boron, the orginal paper[14] should be consulted. As time permits, a vibrational analysis of the bands will be carried out to determine if the bands do correspond to B_2O.

In general, it can be said that the gas phase oxidation of elemental boron is limited by the rate of volatilization of the metal. The reaction products include a large number of partially oxidized boron compounds, having very fast interconversion rates. The balance between oxygen and boron greatly influences the formation and stability of the desired product, B_2O_3. No evidence was found for a detrimental effect due to the formation of HOBO(g).

The possibility exists that the dissociation of B_2O_3 limits the amount of energy released by the combustion of elemental boron.

D. FUTURE WORK

Work is being done on the gas phase analysis of the reaction between chlorine and boron. Additional work will be done on the systems $B-Cl_2-O_2$ and $B-HCl$. When time permits, an analysis of the bands in the range 3500-3770 Å will be attempted.

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13 ABSTRACT The heat of hydrolysis of lithium doped LMH-2 has been completed and the heat of formation calculated to be -5.25 kcal/mole. A preliminary value for the heat of formation of gaseous CF_3ONF_2 was derived from the heat of explosion of mixtures of the sample and hydrogen. The result, -188.4 ± 2.0 kcal/mole, is about the expected value for this compound. Work on DAHTP, TVOPA and "liquid polymer" is continuing. In the synthesis work, the purification of TVOPA has been continued and a method has been developed which gives satisfactory results. Additional pure CF_3ONF_2 has been prepared for heat of formation measurements. A synthesis procedure for CF_3NF_2 has also been developed.

The volatilization and combustion of elemental boron has been studied by flash pyrolysis - kinetic spectroscopy. The species B and B_2 were detected during the volatilization of the element. The combustion of boron in oxygen showed the presence of BO, BO_2, B_2O_2 and B_2O_3 during the reaction. The flash pyrolysis of H_3BO_3 ($HOBO \cdot H_2O$) showed the presence of OH, and BO_2 indirectly that the species $HOBO$ may dissociate to H and BO_2 at high temperatures. There is some evidence that B_2O_3 dissociates to BO and BO_2 at temperatures above its boiling point.

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	ROLE	WT	ROLE	WT	ROLE	WT
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Heat of formation						
LMH-2						
DAHTP						
TVOPA						
Trifluoromethoxydifluoramine						
Combustion of Boron						
Kinetics of Combustion						
HOBO						

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